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METHODS TO EVALUATE SOLID SURFACE TENSION FOR MILITARY FABRICS

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Surface tension studies have been conducted in order to evaluate techniques to examine military fabrics. Calculation of surface tension for a solid surface has been performed using various mathematical models in order to compare the answers obtained from the different models. Contact angle data were collected for the surfaces paraffin, teflon $^{(R)}$, and polystyrene then analyzed using the models of Zisman, Fowkes, Wu and Good. Dispersion, polar, and total surface tensions were predicted using these models. Factors that determine the appropriateness of which model(s) to use when evaluating an unknown surface, such as a military fabric, are discussed. A brief section is included that pertains to the effect of different types of testing liquids (pure versus mixed) on the final answers obtained for surface tensions.

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PREFACE

This project on modeling of surface tension effects was undertaken during the period November 1986 to September 1987. It was funded under Program Element No. 611102A, Project No. AH52, Task No. 01 and Work Unit Accession No. DA311625.

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INTRODUCTION

The goal of the work reported here is to develop methods to characterize the wettability of military cloth. The ultimate goals are 1) to develop a model incorporating this and other information into an overall scheme, whereby military fabrics in current use can be more accurately evaluated, and 2) to supply information to be incorporated into guidelines for improving future fabrics.

Contact angle work has a long history and is currently a very intense area of scientific endeavor. The amount of available information in this research area is overwhelming, but, unfortunately, important questions concerning the best method of analysis or model to use for laboratory data such as ours still do not have completely satisfactory answers.

The purpose of this work with contact angles is to determine the surface tension or surface free energy of military cloth samples. Various contact angle models have been proposed in the literature based on different approximations concerning the physics of the problem. It is straightforward to use laboratory data and any of these models to obtain a value for the surface tension of a fabric. However, since different models are based on different initial assumptions, it is important to determine which model is most appropriate to use when evaluating each type of solid surface or military fabric.

DETERMINATION OF SURFACE TENSION OF MILITARY CLOTH

A. General Discussion

This section considers the determination of the surface tension of a solid surface (such as a military fabric) using contact angle techniques.

When a liquid drop is resting on a solid surface, the equilibrium contact angle, θ_E, is defined as shown in Fig. 1. Young's equation [1] applies when the atmosphere is saturated with the vapor of the liquid (equilibrium) and when the solid surface is perfectly smooth, homogeneous, and planar.

$$\gamma_{sl} + \gamma_{lv} \cos(\theta_E) = \gamma_{sv}.$$ [1]

The γ's are the solid-liquid (SL), liquid-vapor (LV), and solid-vapor (SV) interfacial tensions (force/length or energy/area). If the interfacial tensions are represented as vector quantities with magnitudes and directions as indicated in Fig. 1 (inset), then Young's equation follows immediately.
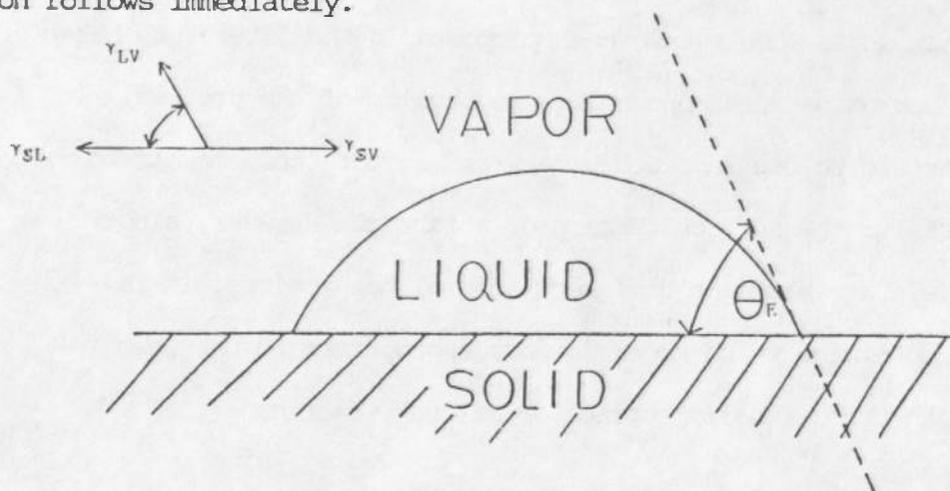
Figure 1. Contact angle, θ_E, for a liquid drop resting on a perfectly smooth, homogeneous and planar solid surface.

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For this work Young's equation is used to obtain information about solid surfaces. The information to be obtained is the solid's surface tension γ_s. The solid-vapor interfacial tension, γ_{sv}, in Young's equation is related to the surface tension of the solid, γ_s, through the solid-vapor equilibrium film pressure, π_E (1).

$$\gamma_s = \gamma_{sv} + \pi_E \, .$$

[2]

This film pressure, π_E, results from adsorption of the liquid vapor on the surface of the solid, thus changing the solid's surface tension and the contact angle. This effect is usually most important only for small contact angles, less than about 10 degrees (1). Many researchers have assumed $\pi_E \approx 0$. This assumption has been made here. Similarly, the effect of any of the vapor of the solid material that might be adsorbed on the surface of the liquid drop is neglected so that the liquid surface tension γ_1 is equal to γ_{1v}. Frequently, γ_1 is simply shortened to γ. Based on these approximations, Young's equation [1] becomes

$$\gamma_{s1} + \gamma_1 \cos(\theta_E) = \gamma_s \, .$$

[3]

It is important to note, that increasingly, workers have discovered that π_E may not be negligible (2). This fact is of concern here, since these experiments were conducted in an open room. Under these conditions there is the possibility of film pressure effects.

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In order to investigate the solid-vapor film pressure effect, an experiment was conducted to determine whether we could detect this effect with our apparatus. In this experiment we looked for differences in the contact angle of a liquid drop placed on a solid surface in a normal room environment versus the same solid surface that had been standing for several days in a closed container with a reservoir of the testing liquid (3). This experiment represented an initial attempt to address the issue of π_E but by itself did not yield enough information to draw definitive conclusions. Additional experiments comparing the effect of different testing liquids on the same solid surface need to be performed.

In addition to film pressure effects, the question of surface roughness is important for this work since a woven fabric sample is obviously not a smooth, homogeneous surface. Work is currently in progress in this laboratory concerning how to account for roughness when determining surface energy of military fabrics. Many articles have been published concerning the topic of surface roughness (for example, Ref. 4). Although we have not to date attempted to characterize surface roughness in terms of fractal concepts, this approach might be a fruitful avenue to explore.

The experimental set-up used to measure contact angles is described in reference 5. The idea was to magnify the image of the liquid drop and then view it through a TV camera. The baseline width (W), the diameter of the drop at the liquid-solid interface, and height (H) of the drop are measured on the TV monitor.

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After the liquid drop has been placed on the solid surface, the timing of the experimental measurement can be important. Our measurements were taken immediately after the drop was placed on the surface. The contact angle, θ_E, is calculated using the relationship

$$\text{TAN} \; (\; \theta_E/2) = (2H/W) \; .$$

[4]

Derivation of this formula (3) is based on the assumption that the drop's surface is perfectly spherical. Contact angle data is given in Appendix A.

The surface tension values of the pure liquids that we used in this work were taken from the literature. See Appendix B for these γ_l values and their literature sources. Surface tensions of the mixed liquids (water/ethanol) were taken from the literature but were also measured in this laboratory using a du Nouy tensiometer (5). The measured values compared well with literature values (5).

The following treatment of the contact angle data is divided into two parts. The first section, Part B, deals with some of the models found in the literature that are used to analyze laboratory data and obtain a value for γ_s. They include the Zisman plot, the Fowkes equation and Extended Fowkes equation (geometric mean), the harmonic mean approximation with and without polar terms, the polarizability model, and the equation of state. Young's equation is fundamental to all of these models. With the exception of the Zisman method, which is

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essentially a plot of the raw data, these different models consist of approximations and/or assumptions about the nature of the interactions between the solid and liquid γ_{sl}. This first part will briefly explain each model and illustrate how it can be used to obtain the surface tension, γ_s, of a solid surface such as a military cloth sample. We are in the initial stages of examining these models and deciding which model(s) will give the most useful or accurate information for the surface tension, γ_s. We have used known surfaces (paraffin, teflon, and polystyrene) and pure liquids to examine the models.

The second section, Part C, pertains to a recently completed technical report (6) in which two of the models, the Fowkes equation and the polarizability model, were used to analyze data for military cloth samples. Using data for the same three surfaces studied in part B (paraffin, teflon, and polystyrene), part C focuses on the effect of the testing liquid on the final answer obtained for γ_s. Only a very limited examination of this important question can be attempted in this report.

B. Models to Evaluate Data

In equation [3], the quantity we wish to determine is γ_s, the solid surface tension. The experimentally measurable quantities are θ_E, the contact angle, and γ_1, the liquid's surface tension. The solid-liquid interfacial tension γ_{sl} is not readily accessible through experimental measurement. The models presented below illustrate some of the ways in which γ_{sl} is taken into account.

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1. Zisman Plots. In Zisman's pioneering work (7), he did not propose a mathematical expression for γ_{sl}. Instead, he neglected the solid-liquid interfacial tension in his data analysis, although he did note this neglect as a shortcoming of his approach and recognized the importance of explicitly accounting for the solid-liquid interaction γ_{sl}. Zisman characterized solid surfaces by a quantity he termed the critical surface tension (CST), γ_c.

$$\gamma_c \equiv \gamma_{sv} - \gamma_{sl}$$

[5]

In equation [5], neglecting γ_{sl}, γ_c is equal to γ_{sv} and with the neglect of π_E, the critical surface tension is equal to the solid surface tension γ_s.

Using equation [5] along with equation [1], it is evident that γ_c will equal γ_{lv} when θ_E equals zero, i.e., when the liquid "wets" the solid's surface. In a Zisman plot cos (θ_E) is plotted versus γ_l. This plot is not a priori any particular shape, but in some cases it is essentially linear.

Zisman plots were constructed for our data (Figs. 2-7). (This information includes 41 data points for paraffin (decane and nonane were not included because of the small contact angles and large errors associated with these measurements), 20 data points for teflon, and 14 data points for polystyrene (see Appendix A)). All data points are

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included and not just the average value of cos (θ_E) for a particular
liquid surface tension value. For comparison purposes, both linear and
quadratic least squares fits were performed for each solid surface. The
calculated values obtained from these graphs and the fitted curves from
these analyses are given in Table 1.

SURFACE TENSION OF PURE LIQUIDS (mN/m)
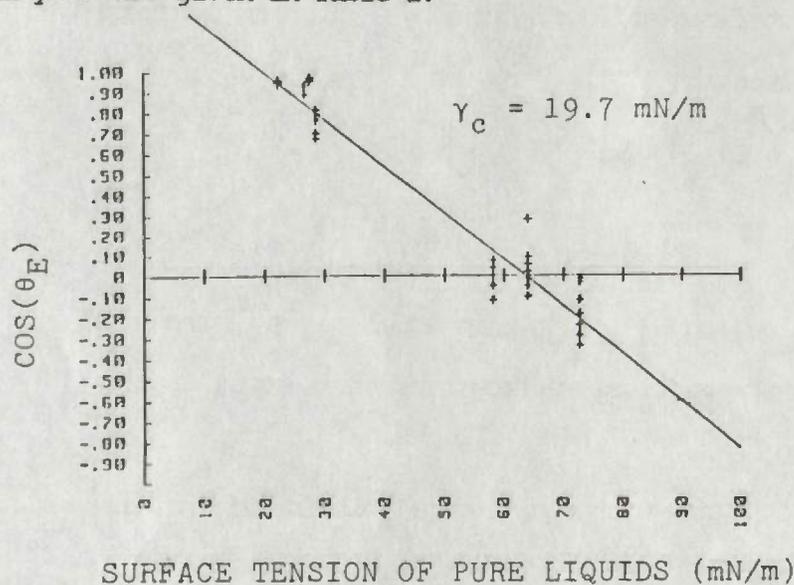
Figure 2. Zisman plot for paraffin. Best fit straight line as
determined by least squares analysis.

SURFACE TENSION OF PURE LIQUIDS (mN/m)
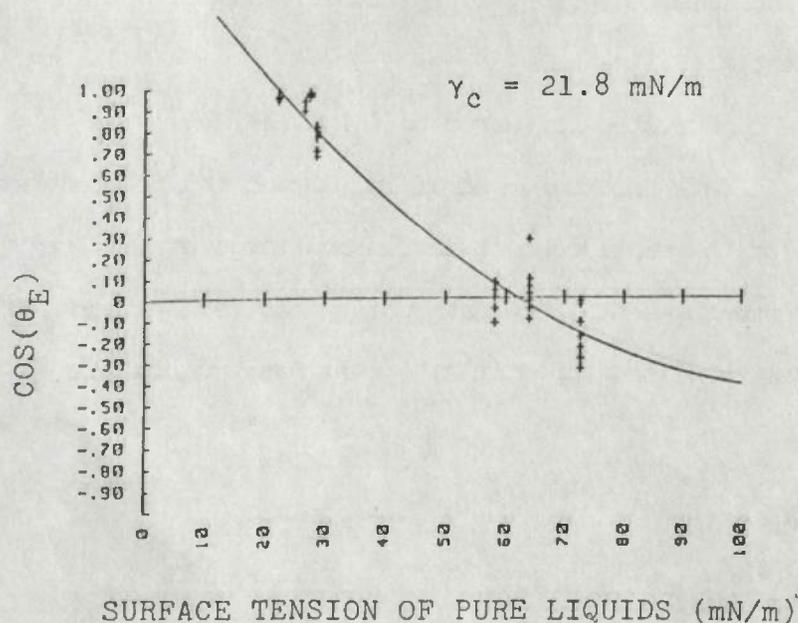
Figure 3. Zisman plot for paraffin. Best fit quadratic curve
as determined by least squares analysis.

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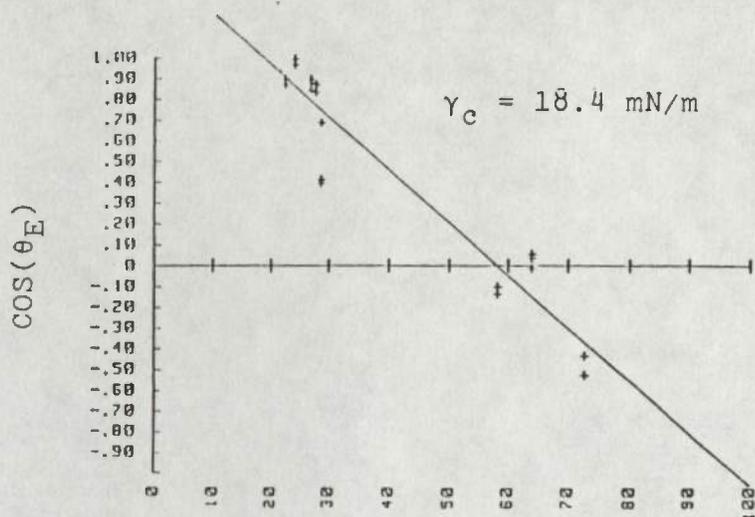
Figure 4. Zisman plot for teflon. Best fit straight line as determined by least squares analysis.
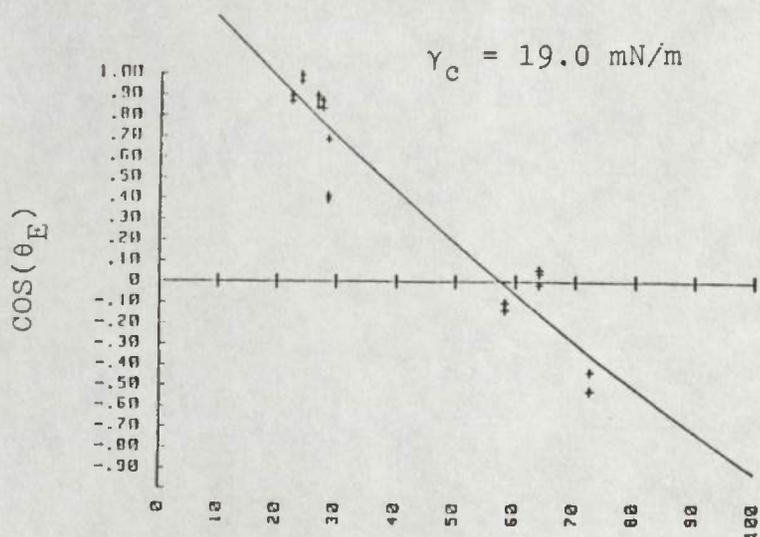
Figure 5. Zisman plot for teflon. Best fit quadratic curve as determined by least squares analysis.

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γ_c = 23.2 mN/m

COS(θ_E)
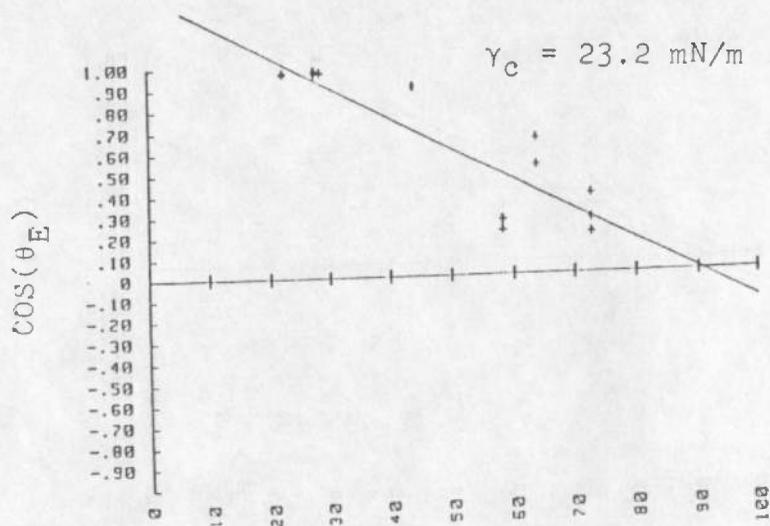
SURFACE TENSION OF PURE LIQUIDS (mN/m)

Figure 6. Zisman plot for polystyrene. Best fit straight line as
determined by least squares analysis.

γ_c = 24.3 mN/m

COS(θ_E)
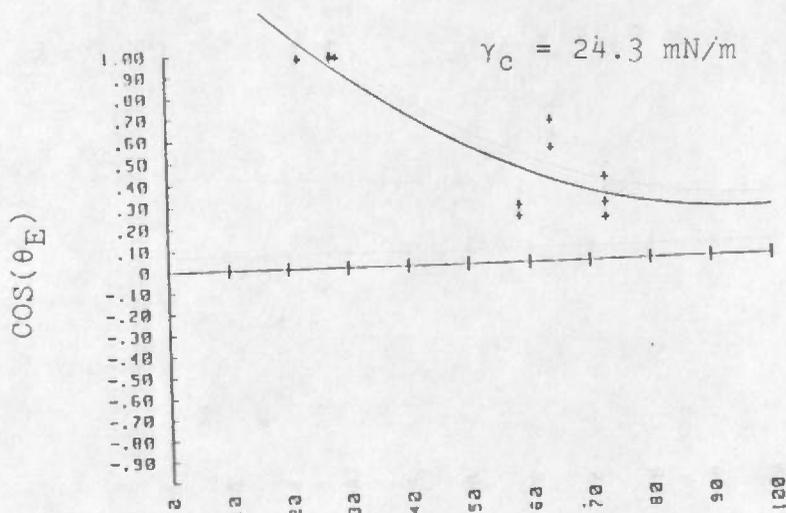
SURFACE TENSION OF PURE LIQUIDS (mN/m)

Figure 7. Zisman plot for polystyrene. Best fit quadratic curve
as determined by least squares analysis.

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TABLE 1. Results of Zisman Analyses for Critical Surface Tension

Solid Surface	γ_c(mN/m)	γ_c(mN/m)
	Linear Fit	Quadratic Fit
Paraffin	19.7 (0.946)	21.8 (0.950)
Teflon	18.4 (0.908)	19.0 (0.909)
Polystyrene	23.2 (0.849)	24.3 (0.856)

The square of the correlation coefficient is shown in parenthesis in Table 1. There is essentially no statistical preference shown for a linear versus a quadratic fit for any of the surfaces. Approximately the same value for the critical surface tension is obtained with linear and quadratic fits, the quadratic fit giving a slightly higher value.

2. Geometric Mean Approximation

In the geometric mean approximation (and in the harmonic mean approximation discussed in a later section), to obtain a mathematical expression for γ_{sl} in terms of known quantities, the assumption is made that the solid surface tension γ_s can be separated into components.

$$\gamma_s = \gamma_s^d + \gamma_s^p \qquad [6]$$

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In equation [6], $\gamma_s{}^d$ is the dispersion component and $\gamma_s{}^p$ is the polar component of the solid's surface tension. Similarly, it is assumed that the liquid's surface tension has dispersion and polar parts which are additive. The dispersion component for any solid or liquid is always nonzero. The polar component for the three surfaces we have examined is zero or very small for paraffin and teflon, but nonzero for polystyrene. Evidently, the optimum condition for spreading and adhesion occurs when the dispersion and polar components of the liquid are similar in magnitude to the dispersion and polar components of the solid.

Fowkes (8) made the assumption that the interaction between the solid and liquid could be approximated by the geometric mean, $\sqrt{\gamma_1{}^d \gamma_s{}^d}$. In his original arguments he considered only the dispersion components. This idea has been extended by others to include polar interactions (1, 9). Consequently, the monolayer of solid molecules at the solid-liquid interface will have the expected solid surface tension, γ_s, but reduced because of the interaction between the solid and liquid by an amount ($\sqrt{\gamma_1{}^d \gamma_s{}^d} + \sqrt{\gamma_1{}^p \gamma_s{}^p}$). The resulting tension of this monolayer of solid material is then ($\gamma_s - \sqrt{\gamma_1{}^d \gamma_s{}^d} - \sqrt{\gamma_1{}^p \gamma_s{}^p}$). Similarly, the tension γ_1 of the liquid monolayer at the interface is assumed to be reduced by the same amount. The sum of these two tensions is the solid-liquid interfacial tension in the geometric mean approximation

$$\gamma_{sl} = \gamma_s + \gamma_1 - 2\sqrt{\gamma_s{}^d \gamma_1{}^d} - 2\sqrt{\gamma_s{}^p \gamma_1{}^p}. \qquad [7]$$

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When equation [7] is substituted into equation [3], the <u>Extended Fowkes</u> <u>equation</u> [8], results

$$\cos(\theta_E) = (2\sqrt{\gamma_s^d \gamma_1^d})/\gamma_1 + (2\sqrt{\gamma_s^p \gamma_1^p})/\gamma_1 - 1 \ .$$

[8]

If the term in equation [8] with the polar components can be neglected (either γ_s^p or γ_1^p negligible or zero), then the <u>Fowkes equation</u> [9], is obtained.

$$\cos(\theta_E) = (2\sqrt{\gamma_s^d \gamma_1^d})/\gamma_1 - 1 \ .$$

[9]

a. <u>Data analysis using Fowkes equation.</u> The surface property which is obtained from a Fowkes analysis is the dispersion component γ_s^d of the solid's surface tension. This information can be obtained from equation [9] by plotting $\cos(\theta_E)$ versus $\sqrt{\gamma_1^d}/\gamma_1$.
According to this model, such a plot should be linear with an intercept of -1 and a slope of $2\sqrt{\gamma_s^d}$.

When using equation [9], the initial problem is to determine the dispersion and polar components of each testing liquid so that these liquids can be used in turn to characterize the unknown solid surfaces of interest (for example, military cloth). A standard approach (10,11) has been to use paraffin, which is assumed to have no polar component of surface tension. Then, for paraffin the dispersion component γ_s^d equals the total tension γ_s, and is assigned a value 25.5 mN/m. Then, rearranging equation [9] we have

$$\gamma_1^d = (\gamma_1 (\cos(\theta_E)+1)/2 \sqrt{25.5})^2 \ .$$

[10]

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$\gamma_1{}^d$ values calculated using equation [10] along with the
corresponding $\gamma_1{}^p$ values ($\gamma_1{}^p = \gamma_1 - \gamma_1{}^d$) are
given in Table 2 under the column heading geometric mean.

TABLE 2. Characterizing Pure Liquids Using 25.5 mN/m for Paraffin

LIQUID	γ_1	θ_{Ave}	GEOMETRIC MEAN		HARMONIC MEAN	
			$\gamma_1{}^d$	$\gamma_1{}^p$	$\gamma_1{}^d$	$\gamma_1{}^p$
	mN/m	Degrees	mN/m	mN/m	mN/m	mN/m
Tetradecane	26.7	24.0	25.6	1.10	25.6	1.10
Decane	23.9	9.00	22.1	1.80	22.2	1.70
Nonane	22.9	4.50	20.5	2.40	20.7	2.20
Iso-octane	18.8	spread				
Heptane	20.3	spread				
Hexane	18.4	spread				
Glycerol	64.0	89.0	41.6	22.4	45.0	19.0
Formamide	58.3	90.8	32.4	25.9	33.0	25.3
Ethylene glycol (monoethylether)	28.6	46.6	22.8	5.80	22.9	5.70
2-Ethoxyethanol*	28.6	38.4	25.5	3.10	25.5	3.10
Ethanol	22.3	20.2	18.3	4.00	18.8	3.50
Benzene	27.6	17.0	28.6	-1.00**	28.7	-1.10**
Water	72.8	101	34.0	38.8	34.9	37.9

*The same chemical as ethylene glycol (monoethylether) but from a
different source.
**Set equal to zero when required for any calculations.

At this point, now that the testing liquids have been characterized, equation [9] can be used again, but, this time, to characterize the solid surfaces, teflon and polystyrene.

Fowkes plots were constructed for our data for teflon and polystyrene (Figs. 8 and 9). (Twenty data points exist for teflon and 14 for polystyrene, see Appendix A). Based on the data points, the best straight line in the least squares sense constrained to pass through an ordinate of -1 was determined. This analysis shows that for our data γ_s^d for teflon is 22.5 mN/m.

Both polystyrene and some of our testing liquids have polar components. Polar terms are not included in equation [9], and this brings into question the appropriateness of using the Fowkes analysis in this situation. This is reflected in Fig. 9 where our data do not appear to be approaching an ordinate of -1. This feature can be seen even more clearly in Figs. 16 and 17 in a later section of this report. In Fig. 16, which is a Fowkes plot for teflon, the data are approaching an ordinate close to -1, while in Fig. 17, which is a Fowkes plot for polystyrene, the data clearly are not approaching an ordinate of -1.
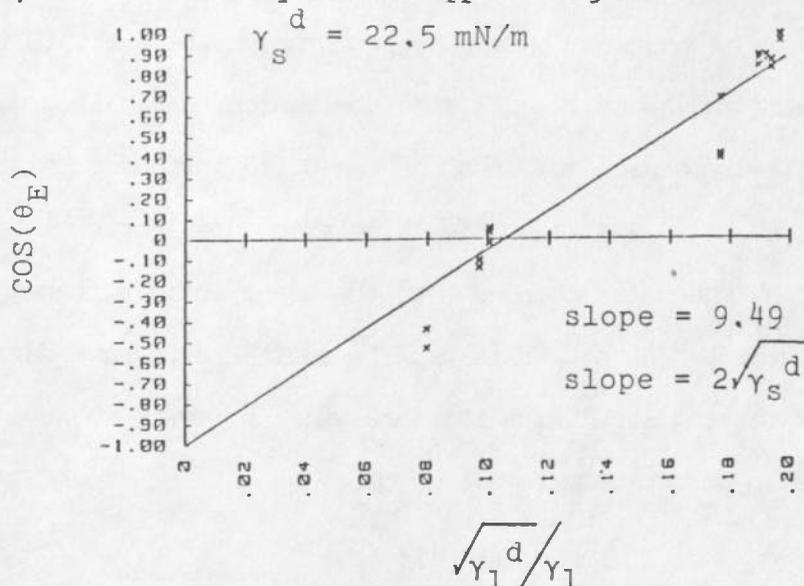
Figure 8. Fowkes plot for teflon. Best fit straight line through an ordinate of -1 as determined by least squares analysis.

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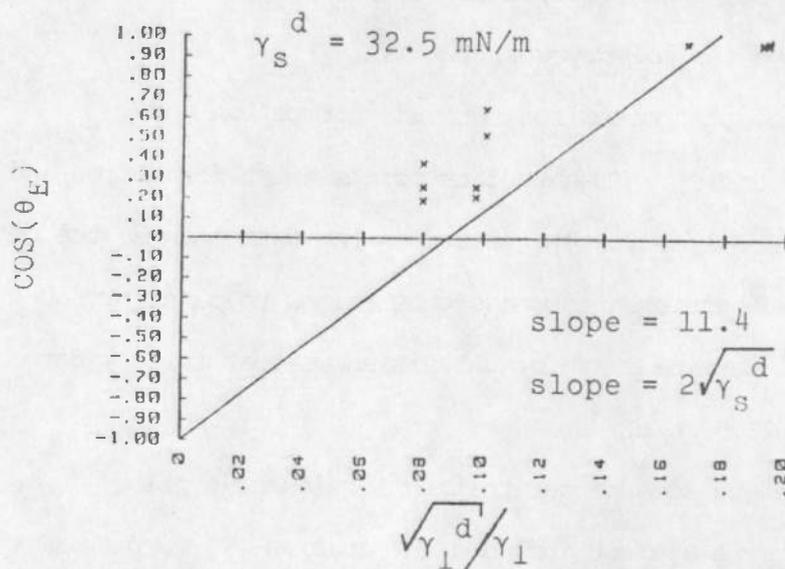
Figure 9. Fowkes plot for polystyrene. Best fit straight line through an ordinate of -1 as determined by least squares analysis.

We can use the Fowkes model to obtain information about polystyrene if nonpolar liquids are used ($\gamma_1^p = 0$). We have data from one liquid which according to our calculations has a negligible polar component and also had a nonzero contact angle on polystyrene. This is benzene. See Table 2 and Appendix A. Using the benzene data along with equation [9] gives a dispersion component of the solid surface tension γ_s^d for polystyrene of 25.8 mN/m. This calculation does not yield any information about the polar component or the total solid surface tension for polystyrene. (Note: It is usually advisable to have data from more than one testing liquid for this analysis; however, we have only one test case in our current data.)

The Fowkes model has been used when both the solid and liquid have polar components, for example, by Saito and Yabe (9) in their analysis of the polystyrene surface. The appropriateness of this analysis would depend on the magnitude of the polar components of the testing liquids, smaller values being the best. For purposes of illustration all of our data could be considered in a Fowkes analysis of polystyrene. Including all of our data in a Fowkes plot we obtain a γ_s^d value of 32.5 mN/m. Because of the limitations of this particular model, the previous value of 25.8 mN/m is a more appropriate figure.

Finally, it should be noted that Saito and Yabe (9) used a γ_s^d value for their paraffin surface of 24.8 mN/m rather than the 25.5 mN/m used here. They obtained this value by using "standard" liquids (n-alkanes) and equation [9] to characterize their paraffin surface.

b. Data analysis using extended Fowkes equation. When both the testing liquid and the solid have a polar component the extended Fowkes equation [8] is applicable. If the dispersion and polar components (γ_1^d and γ_1^p) are known for any one testing liquid and the contact angle θ_E is measured, then equation [8] presents us with one equation and two unknowns (γ_s^d and γ_s^p), and there is insufficient information to solve the problem. One way to overcome this problem is to use the data from two testing liquids. This presents us with the standard algebraic problem of two equations and two unknowns.

An important point for consideration is that there can be variability in the data and that information derived from one pair of testing liquids can give somewhat different answers for γ_s^d and γ_s^p than information from a different pair of testing liquids. It

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has been suggested (9) that this variability depends upon the relative magnitudes of the dispersion and polar components of the two testing liquids. One approach to obtain information about the surface of interest is to examine pairs of testing liquids that give a range of surface tension values and then to take the average value. Another procedure is to find a pair of liquids which give surface tension values close to the average and then use this pair for all subsequent contact angle measurements. As an example, Saito and Yabe (9) found that the two liquid pairs methylene iodide/water and tricresyl phosphate/water gave surface tension values that were close to the average for 12 liquid pairs for polyethylene and polystyrene. Therefore, they used these two liquid pairs to characterize other surfaces.

Our data for teflon and polystyrene have been examined in two ways. The first is by using liquid pairs with two equations and two unknowns for the different liquid pairs and then taking the average value. The second is by a least squares analysis similar to the Fowkes analysis presented in section (a) above and discussed in section (ii) below.

A third method to obtain surface information from equation [8] is possible with an algebraic rearrangement. A linear plot can be obtained with a slope of γ_s^p and ordinate intercept of γ_s^d. For this third method of analysis the dependent variable would be $(\gamma_1 (\cos(\theta_E) + 1)/2 \sqrt{\gamma_1^d})$ and the independent variable would be $(\sqrt{\gamma_1^p}/\sqrt{\gamma_1^d})$. This method of analysis was not examined here, but is a possiblity for future data analysis.

    (i) Liquid Pairs. For teflon we obtained contact angle data for 8 liquids and for polystyrene for 6 liquids (see Appendix A). For the teflon surface analysis benzene was not included, leaving a total of 7 liquids to evaluate this surface. This gives a total of 21 liquid

pairs for teflon and 15 liquid pairs for polystyrene. All of these
liquid pairs were used for each surface along with equation [8] to
calculate the surface tensions and then the averages were taken. The
results for the teflon surface dispersion, polar, and total surface
tensions are 13.7, 15.5, and 29.3 mN/m, respectively, and for
the polystyrene surface are 19.1, 57.1, and 76.3 mN/m. Compared to
literature values, the dispersion components are too small, the polar
components are too large and the total components are too large for each
of the two surfaces.

As discussed by Wu (1), Kaelble has suggested a method to improve
this type of analysis. For two test liquids, 1 and 2, we can define a
parameter D. First, take the square root of the product of the polar
component of liquid 1 and the dispersion component of liquid 2. Then
take the square root of the product of the polar component of liquid 2
and the dispersion component of liquid 1. Finally, subtract the first
quantity from the second and this is the parameter D. The next step is
to calculate D for all liquid pairs. Only those pairs for which D has
an absolute value greater than 10 are included in the analysis. When
our data are examined in this manner teflon is predicted to have
dispersion, polar and total components of 15.2, 4.7, and 19.9 mN/m,
respectively, and polystyrene of 25.4, 7.1, and 32.5 mN/m. It is clear
that using this method to select which liquid pairs to use in the
analysis gives a definite improvement to the values obtained for the
solid surface tensions.

(ii) Least squares. In the previous section of this report,

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when considering the Fowkes equation [9], a least squares analysis was performed and one unknown parameter $2\sqrt{\gamma_s^d}$ was determined based on equation [9] and the surface data. When performing the extended Fowkes analysis, this same approach can be applied to equation [8], but instead of one undetermined parameter, now there are two $(2\sqrt{\gamma_s^d}$ and $2\sqrt{\gamma_s^p})$ to be determined by least squares analysis. The two parameters predicted by statistical analysis for each surface are given in Table 3 (based on 20 data points for teflon and 14 data points for polystyrene; see Appendix A).

TABLE 3. Extended Fowkes Least Squares

Surface	$2\sqrt{\gamma_s^d}$	$2\sqrt{\gamma_s^p}$
Teflon	9.87	-1.14
Polystyrene	9.70	4.39

The result for teflon is a dispersion component of 24.4 mN/m and a polar component of 0.32 mN/m. For polystyrene the dispersion component is 23.5 mN/m and the polar component is 4.8 mN/m.

3. Harmonic Mean Approximation. Wu (1) has proposed approximating the interaction between the solid and liquid using the harmonic mean instead of the geometric mean and suggests that this approximation is an improvement over the geometric mean for studying low energy surfaces. Water-resistant fabrics would be expected to fall into this low energy category.

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Measurements on several experimental films of interest to the military suggest that these films have a surface tension of about 20 mN/m (similar to the value of teflon) (6) Other measurements suggest that Quarpel-treated Nyco has a surface tension even lower than that of the experimental films (6).

The development here is exactly the same as that presented for the geometric mean in Section 2 of this report except that the geometric mean $\sqrt{\gamma_s^d \gamma_1^d}$ is replaced by the harmonic mean $2\gamma_s^d \gamma_1^d / (\gamma_s^d + \gamma_1^d)$.

For the same pair of numbers, taking a harmonic mean gives an answer equal to or smaller than would be obtained with the geometric mean. Therefore, the surface tension of the molecular layers at the solid liquid interface will be reduced by a smaller amount in this approximation than would be the case when using the geometric mean. Analogous to equation [7], which gives the solid-liquid interfacial tension for the geometric mean, the solid-liquid interfacial tension in the harmonic mean approximation is

$$\gamma_{sl} = \gamma_s + \gamma_1 - 4\gamma_s^d \gamma_1^d / (\gamma_s^d + \gamma_1^d)$$
$$- 4\gamma_s^p \gamma_1^p / (\gamma_s^p + \gamma_1^p).$$

[11]

Substituting equation [11] into equation [3] produces the harmonic mean equation with polar terms.

$$\cos(\theta_E) = 4\gamma_1^d \gamma_s^d / [\gamma_1(\gamma_1^d + \gamma_s^d)]$$
$$+ 4\gamma_s^p \gamma_1^p / [\gamma_1(\gamma_1^p + \gamma_s^p)] - 1.$$

[12]

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If the polar terms can be neglected then the _harmonic mean equation_ _without polar terms is obtained._

$$\cos(\theta_E) = 4\gamma_1^d\gamma_s^d/[\gamma_1(\gamma_1^d + \gamma_s^d)] - 1 .$$

[13]

a. _Data analysis using harmonic mean equation without polar terms._
Starting with γ_s^d for paraffin as 25.5 mN/m the dispersion and
polar components of the testing liquids can be determined in the
harmonic mean approximation by rearranging equation [13]

$$\gamma_1^d = \gamma_1\gamma_s^d[\cos(\theta_E)+1]/[4\gamma_s^d - \gamma_1(\cos(\theta_E)+1)] .$$

[14]

Using γ_1 and θ_E values from Table 2, the γ_1^d and
corresponding γ_1^p values ($\gamma_1^p = \gamma_1 - \gamma_1^d$) for
testing liquids can be calculated. These values are listed in Table 2
under the column heading 'harmonic mean'. It can be seen in Table 2
that for these testing liquids, the dispersion and polar components
determined using the geometric versus the harmonic mean approximations
are not identical but that they have similar values.

Using the polar and dispersion components of the liquids calculated
with harmonic mean model along with equation [13] and average values for
θ_E, surface tension values can be obtained for teflon and
polystyrene. The average θ_E values were calculated for each liquid on
each surface from the information in Appendix A. The calculated surface

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tensions are shown in Table 4 for several testing liquids.

TABLE 4. Results for Harmonic Mean Without Polar Terms

Liquid	Teflon(γ_s^d) mN/m	Polystyrene(γ_s^d) mN/m
Tetradecane	24.3	
Decane	25.1	
Glycerol	25.7	57.7
Formamide	20.9	39.5
2-ethoxyethanol	18.5	
Ethanol	23.6	26.2
Benzene	22.9	25.8
Water	12.8	69.3
Ethylene glycol (monoethylether)		36.5

The data in Table 4 give an average value for teflon for γ_s^d of 21.7 mN/m. For polystyrene the only truly appropriate value is the 25.8 mN/m obtained with benzene. The other liquids are polar and their appropriateness to use with this model depends on the magnitude of their polar component (the smaller the polar component, the better the expected results).

It is instructive to note the widely varying values obtained with the polar liquids in Table 4 for polystyrene. For teflon where γ_s^p approximately equal to zero makes all the liquids appropriate within the framework of the model, reasonable and consistent values are obtained for almost all of the testing liquids.

b. Data analysis using harmonic mean equation with polar terms. As with the extended Fowkes equation [8], the harmonic mean equation with polar terms, equation [12], requires information from two testing liquids and is a problem of two equations and two unknowns. Solving these equations is not conceptually difficult, but does require some

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algebraic manipulation. Wu (1) lists a short FORTRAN program, which has

as input the contact angle of two testing liquids and their surface

tensions (total and components) and the output is the dispersion and

polar components of the solid's surface tension. Part of the algebraic

manipulation involved in solving this problem requires using the

quadratic formula. As a result, the output of the program actually

consists of two solutions to the same problem, only one of which is

"significant," meaning physically reasonable and applicable to the

particular surface of interest. Some results obtained from our data

using this computer program are listed in Table 5. Both solutions

obtained from the program are given in the table. It is not obvious

which solution is the physical one for every case.

TABLE 5. Results for Harmonic Mean with Polar Terms

	TEFLON			POLYSTYRENE		
	γ_s^d	γ_s^p	γ_s	γ_s^d	γ_s^p	γ_s
LIQUID PAIR		mN/m			mN/m	
Tetradecane	22.4	1.05	23.4			
and Decane	29.6	-.585	29.0			
Decane and	21.1	2.22	23.4			
Glycerol	26.2	-.209	26.0			
Formamide,	14.3	3.20	17.5			
2-ethoxyethanol	24.1	-1.09	23.0			
Benzene,	11.3	.890	12.1	30.8	8.38	39.2
Water	26.0	-4.82	21.2	58.8	1.36	60.2
Tetradecane,	21.8	1.82	23.7			
Glycerol	26.7	-.388	26.3			
Glycerol,	12.4	10.2	22.6			
2-ethoxyethanol	30.1	-1.55	28.6			
Glycerol,	14.0	8.10	22.1			
Ethanol	27.1	-.530	26.6			
Formamide,	19.5	.561	20.1			
Benzene	25.0	-1.34	23.6			
2-ethoxyethanol	16.8	.727	17.6			
Benzene	24.8	-1.16	23.7			
Formamide				21.6	6.09	27.7
Ethyleneglycol (monoethylether)				44.0	-.839	43.1
Glycerol				14.5	56.5	71.0
Ethyleneglycol (monoethylether)				70.7	-2.07	68.7
Glycerol,				30.6	11.3	41.9
Benzene				51.3	1.43	52.7

Apparently, Wu (1) intended that negative solutions be rejected.

However, if a surface tension has a negative sign, as for example some of

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the polar components for teflon, but has a very small magnitude, then perhaps this negative value is the result of experimental error and/or shortcomings of this particular mathematical model. The best solution for the dispersion component could be matched with this particular negative polar component. For example, the liquid pair formamide/ 2-ethoxyethanol gives a polar component of -1.09 mN/m. However, the dispersion component is 24.1 mN/m, a reasonable value for teflon. The second solution for this same liquid pair is 14.3 mN/m for the dispersion component and 3.20 mN/m for the polar component. The dispersion component of this second solution is not consistent with the accepted value for teflon. Also for some of the data (liquid pairs), this program could give no solution. The reason for this is that this model predicts that the surface tension has a very small imaginary part and the program could not handle this situation (although it would be possible to modify the program to do this). For teflon with the liquid pair tetradecane/ethanol for our data this model predicts $\gamma_s^d = 23.4 \pm .749i$ and $\gamma_s^p = .303 \mp .347i$. If the imaginary parts are neglected, the real part of the solutions give a good value for the teflon surface. This method of analysis could be promising but we need to better understand how to interpret the results.

As we pointed out previously with respect to the geometric mean method, the success of the data analysis depends on using appropriate testing liquids. In his discussion of the harmonic mean method, Wu (1) suggests that the liquid pair water and methylene iodide are 'convenient' testing liquids. We need to know which liquids are best to characterize our surfaces.

4. Polarizability Model or Equation of State

In the previous sections of this report, the objective has been to

solve equation [3] for the solid surface tension γ_s. The difficulty
has been to find a reasonable approximation for the solid-liquid
interfacial tension γ_{sl}. The idea has been to separate the liquid
and solid surface tensions into dispersion and polar components,
equation [6], and then to use the geometric or the harmonic mean to
account for the interfacial effects.

Physically, on the molecular level, what is occurring and what
specific forces can account for our macroscopic observations? Much work
has been done and is being done to answer this question (12).

Good (13) and Girifalco have attempted to answer the question.
Their approach has been to suggest an expression for the solid-liquid
interfacial tension, as has been done in equations [7] and [11] for the
geometric and harmonic means, but their expression takes on a somewhat
different form:

$$\gamma_{sl} = \gamma_1 + \gamma_s - 2\phi\sqrt{\gamma_1\gamma_s}.$$

[15]

The molecular interactions are accounted for in the ϕ function.
Included explicitly in this function are interactions between the solid
and liquid molecules due to dipole orientation, induction effects and
London dispersion forces. Good has attempted to correlate and compare
this theory with the geometric mean approximation (11).

When equation [15] is substituted into equation [3], the result is

$$\cos(\theta_E) = 2\phi\sqrt{\gamma_s/\gamma_1} - 1.$$

[16]

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Equation [16] can be rewritten

$$\cos(\theta_E) = 2\sqrt{\gamma_c / \gamma_1} - 1,$$ [17]

where γ_c is an approximation to the solid surface tension and is a function of ϕ.

a. Polarizability model. De Gennes (12) in a review article considers equation [17] and its implications in terms of the polarizabilities of the solid and liquid. He details research efforts which are of interest in this area.

Our data were analyzed using equation [17] and making the approximation that γ_c is a constant. Plots were constructed of $\cos(\theta_E)$ versus $1/\sqrt{\gamma_1}$. The best least squares line passing through -1 was determined for each plot. The slopes of these lines are $2\sqrt{\gamma_c}$. See Figs. 10, 11, and 12 (based on 41 data points for paraffin, 20 data points for teflon and 14 data points for polystyrene). The surface tensions for paraffin and teflon were found to be 20.0 and 19.1 mN/m respectively. The surface tension for polystyrene was found to be 26.5 mN/m.

b. Equation of state. Equation [17] can be reexpressed in the following form:

$$\gamma_c = [1 + \cos(\theta_E)]^2 \; (\gamma_1/4).$$ [18]
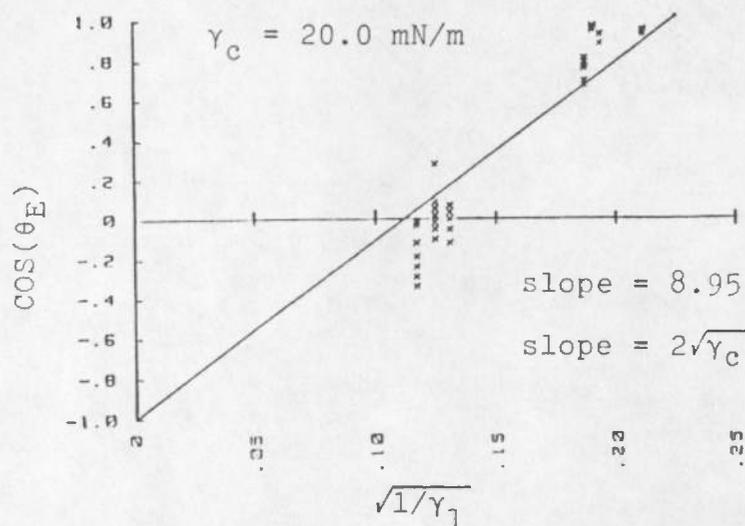
Figure 10. Polarizability model for paraffin. Best fit straight line through an ordinate of -1 as determined by least squares analysis.
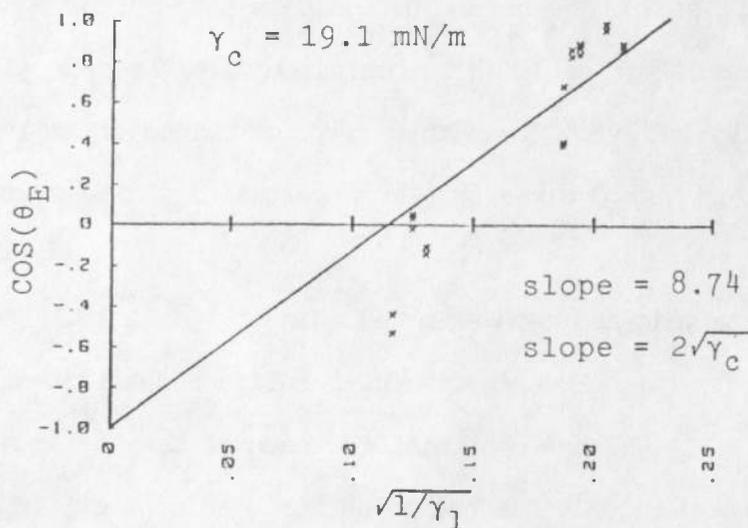
Figure 11. Polarizability model for teflon. Best fit straight line through an ordinate of -1 as determined by least squares analysis.

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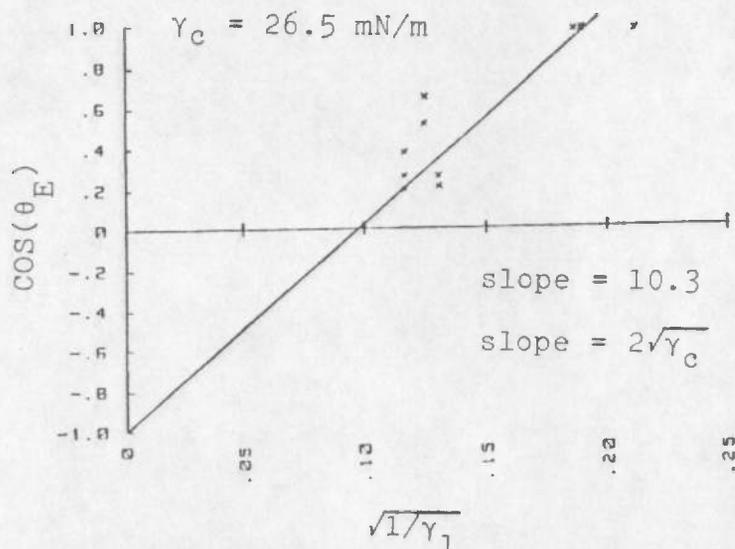
Figure 12.   Polarizability model for polystyrene. Best fit straight
line through an ordinate of -1 as determined by least
squares analysis.

Wu (1) argues that when γ_c is plotted as a function of γ_l, a peak
will be obtained and the peak value (maximum value of γ_c) is the
surface tension of the solid. He refers to equation [17] as the equation
of state. (This nomenclature can lead to confusion since Neumann (14) has
given the name equation of state to another distinct method of analysis.)
Wu (1) claims that this method gives excellent values for solid surface
tensions.

This method of analysis has been examined using our data (5), Dann's
data (10) and Wu's data (1). These plots for paraffin and teflon are shown
in Figs. 13 and 14.   (Fig. 13 has one point for each of the 10 liquids for
paraffin (McDermott) and Fig. 14 has one point for each of the 8 liquids
for teflon (McDermott), see Appendix A). Wu's data for paraffin show a
surface tension of 32.0 mN/m and for teflon of 22.6 mN/m. The value for
paraffin is high compared to the 'standard' 25.5 mN/m. However, Wu claims
the higher number for paraffin is closer to the true value of γ_s (see
Table. 5.1 reference (1)).

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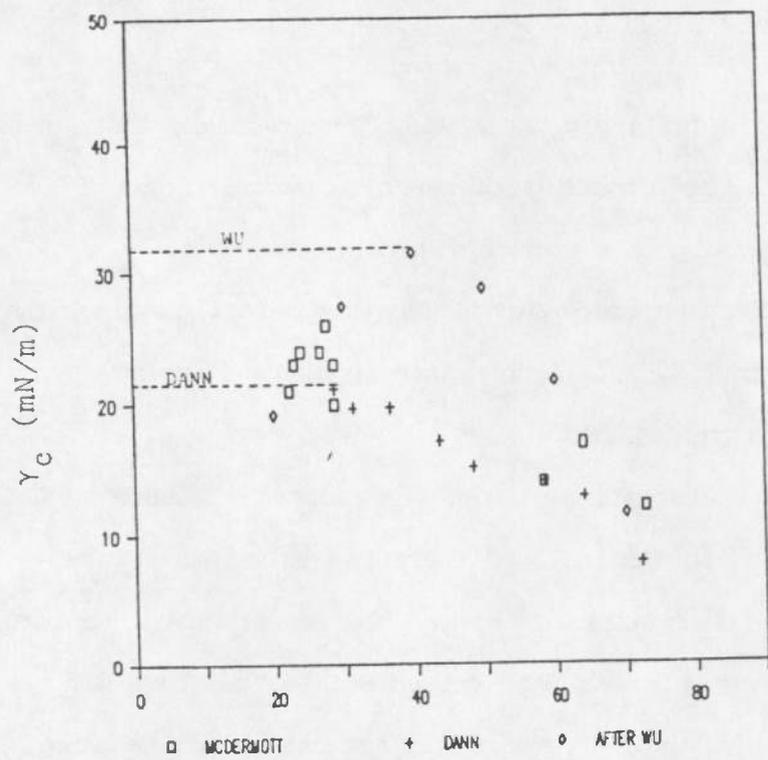
SURFACE TENSION OF TESTING LIQUIDS (mN/m)

Figure 13. Equation of state plot for paraffin. Comparison of three different data sets.
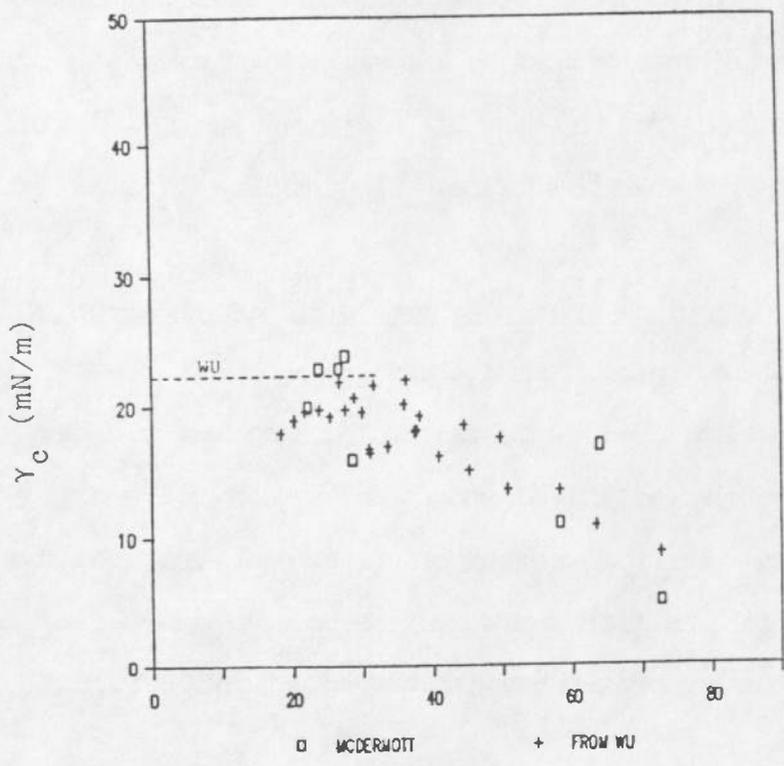
SURFACE TENSION OF TESTING LIQUIDS (mN/m)

Figure 14. Equation of state plot for teflon. Comparison of two different data sets.

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Our liquids (McDermott(5)) did not have surface tension values close enough together over a sufficiently wide range to permit the determination of γ_s using this technique and our own data. Therefore, for comparison purposes Dann's data for paraffin was plotted along with Wu's data in Fig. 13. Dann's data suggests a surface tension of about 22 mN/m using this method.

We see in Fig. 14 that testing liquids with almost the same surface tension values can produce distinctly different γ_c values. This might help explain the discrepancies between the answers obtained for the paraffin surface using Dann's data versus Wu's data. Dann did not analyze his data in this way and perhaps did not use enough testing liquids for this technique to successfully analyze his data. (Note: In Fig. 13, the "data" attributed to Wu was taken from a graph of data and accurately represents his results, but are not actual data points).

Another possible explanation for the discrepancies between the solid surface tensions obtained from the data of Dann and Wu (Fig. 13) could be a difference in their paraffin surfaces, for example, surface roughness.

5. Summary and Comparison of Results from Different Models

The results presented in sections 1-4 are compared in Table 6.

Two models are not included in the table. For the harmonic mean (with polar terms) we need additional understanding concerning how to interpret the results. For the equation of state model as stated above, our data did not contain sufficient information to give reliable values for γ_s (although this report illustrates how to obtain γ_s values using this model).

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TABLE 6. Comparison of Results from Different Models

MODEL (all units in mN/m)	PARAFFIN γ_c	TEFLON				POLYSTYRENE			
		γ_c	γ_s^d	γ_s^p	γ_s	γ_c	γ_s^d	γ_s^p	γ_s
Zisman (linear)	19.7	18.4				23.2			
Zisman (quadratic)	21.8	19.0				24.3			
Fowkes			22.5				25.8		
Extended Fowkes (liquid pairs)			15.2	4.7	19.9		25.4	7.1	32.5
Extended Fowkes (least squares)			24.4	.32	24.7		23.5	4.8	28.3
Harmonic Mean (no polar)			21.7				25.8		
Polarizability	20.0	19.1				26.5			

   a. _Paraffin Results_. Since we used paraffin to obtain the polar and dispersion components of the test liquids, we could not validly use these same liquids to evaluate the paraffin surface in the harmonic and geometric mean calculations. Therefore, the γ_c values were the only information we could obtain concerning our paraffin surface from the Zisman and polarizability models. These values were in good agreement with each other and in reasonable agreement with the literature value of 23 mN/m (1). Wu illustrates with literature data in Table 5.1 of reference 1 that the critical surface tension obtained when using the Zisman model is usually smaller than the surface tension γ_s.

   b. _Teflon Results_. Our γ_c values from the Zisman and polarizability models are in good agreement with each other and with

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literature values; Wu (1) gives a literature value of 18 mN/m.

Literature values (1) for the total surface tension are given as 19.1 mN/m for the geometric mean and 22.5 mN/m for the harmonic mean. Wu (1) shows many examples where the harmonic mean gives a higher value than the geometric mean. This relationship cannot be seen with our limited data. The extended Fowkes method using liquid pairs gave somewhat different answers than when using least squares.

c. Polystyrene Results. The γ_c value for polystyrene as given by Wu (1) is 33 mN/m. Our Zisman results were about 10 mN/m less. The polarizability model is in better agreement with a value of 26.5 mN/m.

Wu (1) gives a total surface tension γ_s for polystyrene of about 42 mN/m. This is about 30% higher than our values. We do not have an explanation for this difference. Additional data and perhaps other models need to be studied.

Polystyrene is an instructive example. It has a polar component of surface tension, which means the intercept in Fowkes plots is not -1. Apparently some of the fabrics examined in a recent technical report (6) also possess polar components since they too did not have intercepts of -1 in the Fowkes plots. In our data analysis we obtain reasonably consistent results for the dispersion component but the predictions for the polar component are not as good. We must learn how to obtain reliable results for both polar and dispersion components for a surface such as polystyrene in order to explain wettability and adhesion in fabrics of interest.

To do this we could initially examine a Fowkes plot. In the absence of a -1 intercept, we could use the extended Fowkes, the harmonic mean (with

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polar terms) or the equation of state models. For each of these methods we need to analyze more laboratory data and/or literature data in order to better understand the results we obtain from a particular model.

B. CONTACT ANGLE DATA USING MIXED LIQUIDS

1. Data Comparison. Contact angle data using ethanol water mixtures on paraffin were compared for the data of Dann (10), Segars (6), McDermott (5) and Good (11). The measured contact angle was plotted versus the percent by volume of alcohol. This data comparison can be seen in Fig. 15. The surface tension of ethanol water mixtures decreases as the concentration of ethanol increases (see Fig. 1 of Ref. 6) and as expected the contact angle decreases with the surface tension. Our data (Segars and McDermott) compare well with the data of Dann and Good. The Segars data were taken with a camera photographic set-up while the McDermott data were taken with a TV camera monitor set-up.
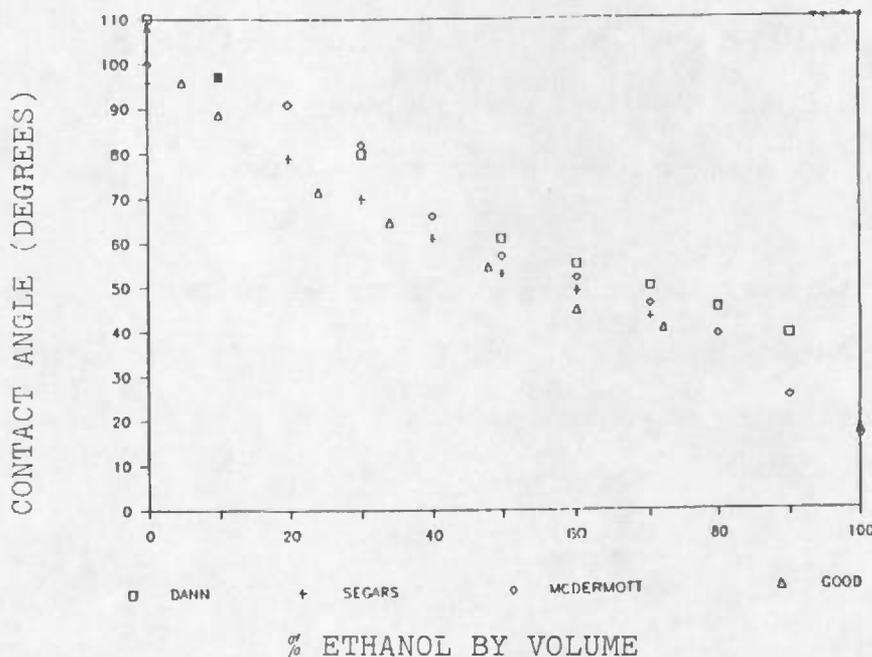

Figure 15. Contact angles on paraffin for different water-ethanol mixtures. Comparison of four different data sets.

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There have been concerns (1, 15) about using mixed liquids, such as water ethanol mixtures, because of a possible preferential adsorption of the ethyl alcohol at an interface. Preferential adsorption could give misleading answers for the solid surface tensions. Since we have evaluated materials using water ethanol mixtures (6) and could find them convenient to use in future research, we need additional information concerning this point. In the next two brief sections of this report, some data concerning pure and mixed liquids are compared using the Fowkes plot and the polarizability model (the two models examined in reference 6).

2. Fowkes Plot Comparing Pure and Mixed Liquids. Since we did not have our own laboratory data available to make this comparison we used literature data from Dann (10). Two surfaces were examined, teflon and polystyrene. A comparison was made among pure liquids, and three types of mixed liquids (Figs. 16 and 17). The mixed liquids were ethanol/water, formamide/2-ethoxyethanol and ethylene glycol/2-ethoxyethanol. Although only a limited amount of data has been considered here, the comparison based on the Fowkes plot shows no apparent differences between the pure and mixed liquids.

It is apparent that the teflon surface is appropriate to the Fowkes analysis since the ordinate intercept of Fig. 16 appears to be approaching -1. This is not true for the polystyrene surface of Fig. 17.

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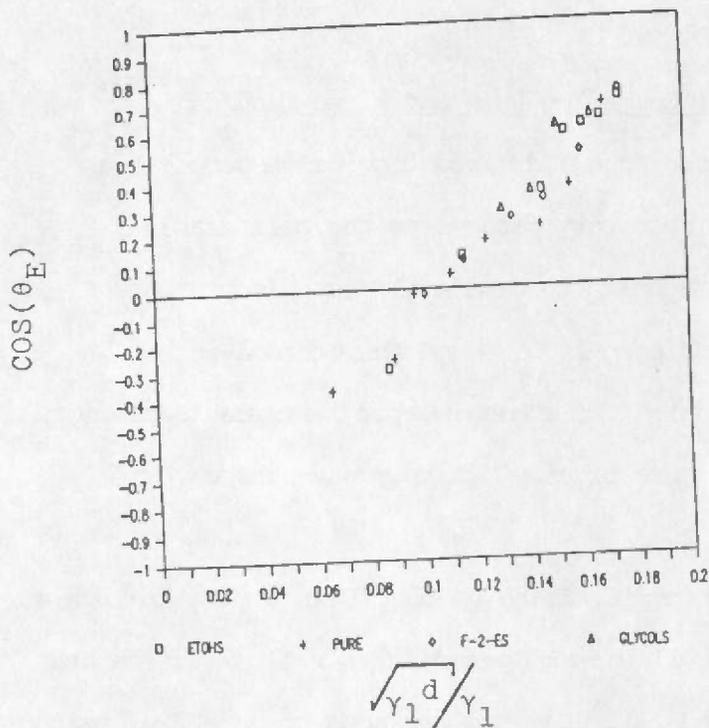
Figure 16.   Teflon: Fowkes plot comparing pure and mixed liquids. Data from Reference 10. Ethanol/water mixtures (ETOHS). Pure liquids (PURE). Formamide/2-ethoxyethanol mixtures (F-2-ES). Ethylene glycol/2-ethoxyethanol mixtures (GLYCOLS).
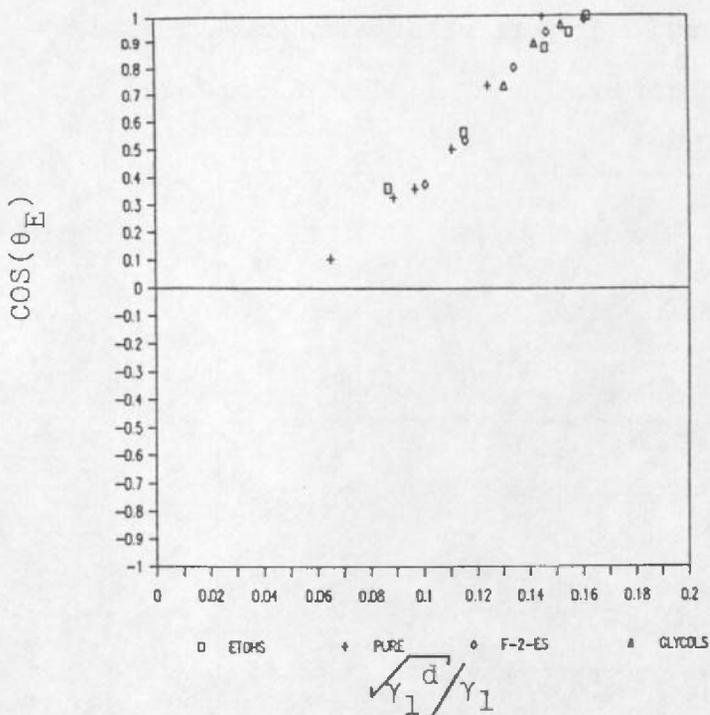

Figure 17.   Polystyrene: Fowkes plot comparing pure and mixed liquids. Data from Reference 10. Ethanol/water mixtures (ETOHS). Pure liquids (PURE). Formamide/2-ethoxyethanol mixtures (F-2-ES).   Ethylene glycol/2-ethoxyethanol mixtures (GLYCOLS).

3. Polarizability Model Comparing Pure and Mixed Liquids. We had

obtained some initial data for pure and mixed liquids on paraffin and

decided to examine our own laboratory data using the polarizability

model (see Fig. 18). There appears to be a small but discernible

difference in the behavior of pure liquids and the ethanol-water

mixtures when using this model. The ethanol-water mixtures 'appear' to

have a slope similar to the pure liquids but they have a smaller

ordinate intercept.

In addition to our data for paraffin, we used Dann's data to look at

other surfaces and different liquids on paraffin as well as teflon and

polystyrene (Figs. 19, 20 and 21). For the surfaces of paraffin, teflon

and polystyrene, the initial observation based on our data holds true;

the ethanol-water mixtures behave somewhat differently than the pure

liquids. However, for some of the other mixtures, the trend is

unclear. It would be instructive to perform a statistical analysis on

the data in Figs. 18-21 to determine the γ_s values for the pure

versus the mixed liquids.
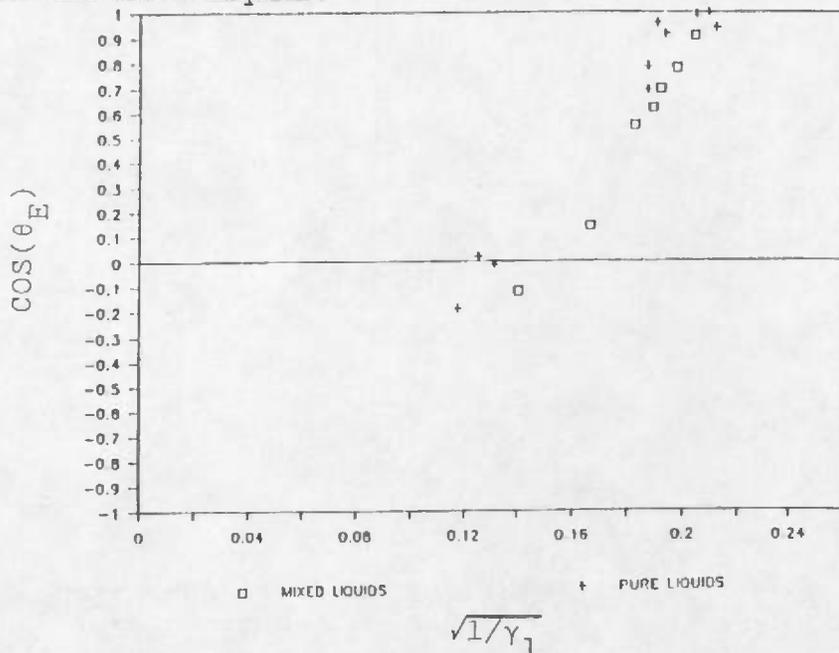
Figure 18. Paraffin: polarizability model comparing pure liquids and ethanol-water mixtures for Natick data.
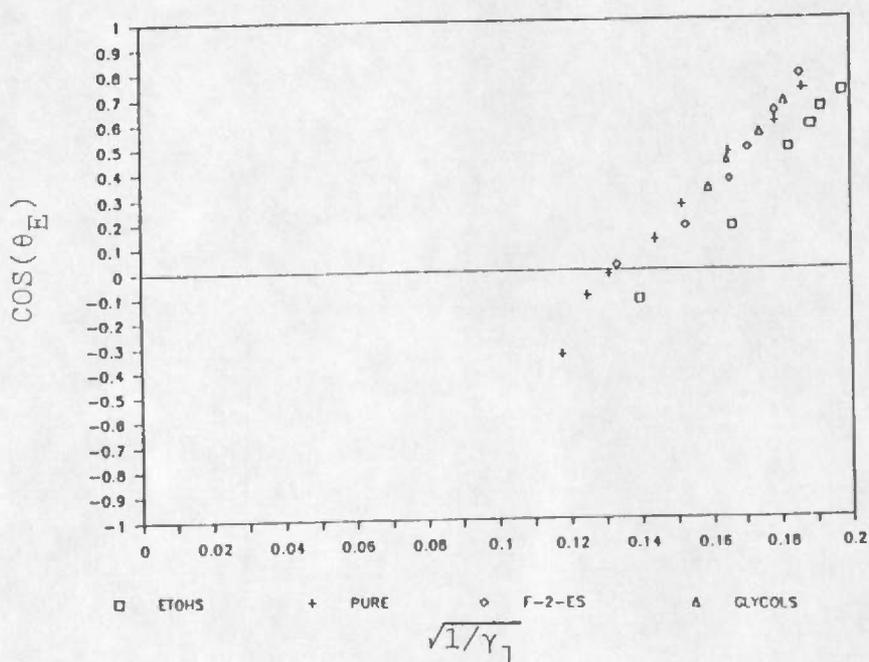
Figure 19. Paraffin: polarizability model comparing pure and mixed liquids for Dann's data. Data from Reference 10. Ethanol/water mixtures (ETOHS). Pure liquids (PURE). Formamide/2-ethoxyethanol mixtures (F-2-ES). Ethylene glycol/2-ethoxyethanol mixtures (GLYCOLS).
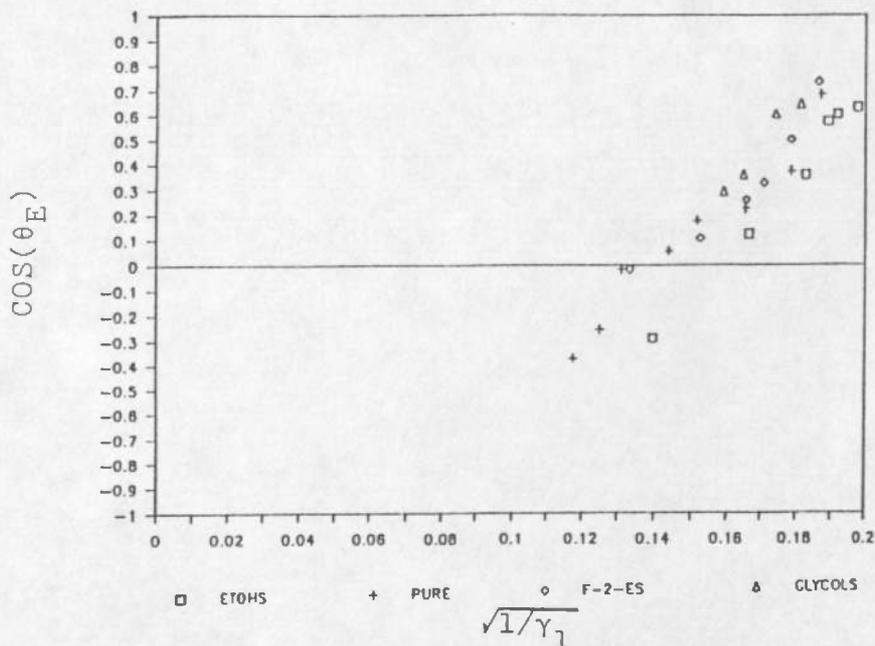
Figure 20. Teflon: polarizability model comparing pure and mixed liquids for Dann's data. Data from Reference 10. Ethanol/water mixtures (ETOHS). Pure liquids (PURE). Formamide/2-ethoxyethanol mixtures (F-2-ES). Ethylene glycol/2-ethoxyethanol mixtures (GLYCOLS).
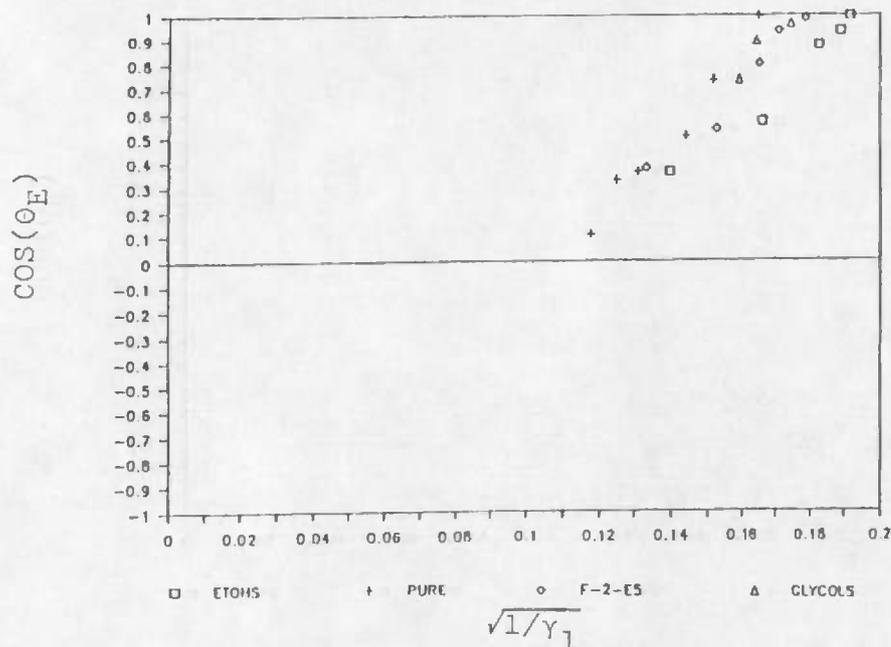
Figure 21. Polystyrene: polarizability model comparing pure and mixed liquids for Dann's data. Data from Reference 10. Ethanol/water mixtures (ETOHS). Pure liquids (PURE). Formamide/2-ethoxyethanol mixtures (F-2-ES). Ethylene glycol/2-ethoxyethanol mixtures (GLYCOLS).

The equations pertinent to both models (Fowkes and polarizability) predict an intercept of -1. However, the two different models can behave very differently with respect to the ordinate intercept for identical data. See, for example, the polystyrene data in Figs. 17 and 21.

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SUMMARY AND CONCLUSIONS

Methods to characterize military cloth with respect to surface tension have been examined. Surface tension evaluation required contact angle measurements for which a technique using a TV camera connected to a monitor was employed (5). Data were obtained easily and quickly using this method. Data for the surfaces paraffin, teflon and polystyrene were collected. These data were analyzed using the mathematical models of Zisman, Fowkes, Wu and Good in order that the different models could be evaluated and compared. As is well known, teflon has a very small (negligible) polar component of surface tension while polystyrene has both polar and dispersion components. The surfaces of military fabrics can be expected to fall into one of these two categories. Therefore, an examination of mathematical models with respect to these surfaces is instructive for application of the models to fabric surfaces. The Zisman method gives a rough estimate of the surface tension and is relatively easy to use. The Fowkes model is more sophisticated and can give the components of the surface tension (dispersion and polar). Wu claims his harmonic mean method is best for low energy surfaces; military fabrics fall into this category. Wu's harmonic mean method can yield dispersion and polar components for the surface tension. However, the meaning of the answers one obtains with the harmonic mean method are not always clear and further work is needed to investigate the usefulness of this model. Wu proposed a second model (equation of state) which we examined using literature data. This model gives only the total surface tension, not the components, but Wu claims the method gives accurate answers. Good's model (polarizability) is

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instructive since it is an attempt to address the issue of interfacial tension and surface tension on the molecular level. This particular model, though, still needs further development.

An examination was made of the use of pure versus mixed liquids with the Fowkes and Good models. The conclusion from the limited data considered is that pure and mixed liquids give the same answers when using the Fowkes model but that there can be differences when using the Good model.

A coherent description of wetting phenomena at a theoretical level has been published (16). In addition, a brief literature review pertaining to military applications is available (17).

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APPENDIX A

TABLE A-1. Raw Data for Contact Angle Measurements

A. PARAFFIN

Test Liquid	Width (m x 10^{-2})	Height (m x 10^{-2})	Angle (degrees)
Benzene	12.7	1.0	18
	12.5	0.9	16
	13.5	0.9	15
	13.2	1.1	19
Ethanol	12.4	1.1	20
	11.3	0.9	18
	11.1	1.1	22
Formamide	8.8	4.4	90
	9.0	4.2	86
	8.5	4.5	93
	8.2	4.6	97
	8.5	4.1	88
2-ethoxy-	12.8	2.2	38
ethanol	12.9	2.1	36
	14.0	2.4	38
	13.9	2.5	40
	13.5	2.5	41
Tetradecane	14.4	1.4	22
	14.3	1.4	22
	15.4	1.9	28
Water	6.9	3.5	91
	7.1	3.7	92
	6.6	4.2	104
	7.1	4.0	97
Water	5.8	3.9	107
(repeat)	6.4	3.9	101
	6.2	4.2	107
	6.0	4.3	110
Ethylene	12.3	2.6	46
glycol	11.7	2.5	46
(mono-	12.4	2.6	46
ethylether)	12.3	2.7	48
	11.8	2.6	48
Glycerol	6.3	3.0	87
	8.5	3.2	74
	6.8	3.1	85
	8.0	3.6	96

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TABLE A-1. Raw Data for Contact Angle Measurements

A. <u>PARAFFIN</u> (Continued)

Test Liquid	Width (m x 10^{-2})	Height (m x 10^{-2})	Angle (degrees)
Glycerol	11.4	5.6	89
(repeat)	8.4	4.3	91
	5.5	2.9	93
	15.1	7.4	89
Hexane	spread		
Heptane	spread		
*Decane	determined with protractor		9
Iso-octane	spread		
*Nonane	determined with protractor		4.5

*Not used in the Zisman or polarizability analysis, but included in the equation of state plot.

B. <u>TEFLON</u>

Test Liquid	Width (m x 10^{-2})	Height (m x 10^{-2})	Angle (degrees)
Water	5.9	4.7	116
	5.6	5.0	122
Benzene	12.6	1.7	30
	12.6	1.9	34
2-ethoxy-	12.5	2.7	47
ethanol	10.2	3.3	66
	10.3	3.4	67
Formamide	9.3	5.2	96
	8.8	5.1	98
Ethanol	14.2	1.9	30
	13.1	1.6	27
Hexane	disappears (absorbed)		
Tetradecane	10.9	1.6	33
	11.0	1.3	27
	11.8	1.5	29

TABLE A-1. Raw Data for Contact Angle Measurements

TEFLON (Continued)

Test Liquid	Width (m x 10^{-2})	Height (m x 10^{-2})	Angle (degrees)
Glycerol	11.7	5.6	87
	14.8	7.2	88
	11.7	6.0	91
Decane	14.3	1.0	16
	16.2	0.6	8
	15.5	1.1	16

C. POLYSTYRENE

Test Liquid	Width (m x 10^{-2})	Height (m x 10^{-2})	Angle (degrees)
Water	8.9	3.4	75
	8.7	3.6	79
	17.2	5.8	68
Decane	spread		
Tetradecane	spread		
Formamide	9.9	3.8	75
	9.7	3.9	78
Glycerol	12.4	2.9	50
	13.8	3.9	59
ETOH	spread	(surface unclean?)	
+*ETOH	18.1	1.1	14
(repeat)	18.0	1.3	16
Benzene	18.6	1.0	12
	18.2	1.3	16
	18.5	1.2	15
Ethylene-	12.6	0.8	14
glycol	11.8	0.8	15
monoethylether			

*Drop had odd shape.
+These two values used in all data analyses. The previous two values (spread) were neglected.

APPENDIX B

Surface Tension of Pure Liquids

Liquid	Surface Tension (mN/m)	Reference
Tetradecane	26.7	18
Decane	23.9	18
Nonane	22.9	18
Iso-octane	18.8	19
Heptane	20.3	18
Hexane	18.4	21
Glycerol	64.0	10
Formamide	58.3	10
Ethylene glycol (monoethylether)	28.6	10
2-ethoxyethanol	28.6	10
Ethanol	22.3	20
Benzene	27.6	21
Water	72.8	10

APPENDIX C

LIST OF SYMBOLS USED

θ_E Equilibrium contact angle

γ_{sl} Solid liquid interfacial tension

γ_{lv} Liquid vapor interfacial tension

γ_{sv} Solid vapor interfacial tension

γ_s Solid surface tension

γ_l Liquid surface tension

π_E Equilibrium film pressure

γ_c An approximation to γ_s

γ_s^d Dispersion component of γ_s

γ_s^p Polar component of γ_s

ϕ Molecular interaction function (Good-Girifalco model)

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